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Ceramic Matrix Composites by Liquid Infiltration

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SUMMARY

This work was done in response to a well recognized need for a more effective process for manufacturing advanced ceramic matrix composites. It is based on a proposal by Applied Sciences, Inc. and the Basic Industry Research Laboratory (BIRL) of Northwestern University to evaluate the feasibility of a new, unique **Liquid Infiltration** process for depositing ceramic matrix materials within woven fiber preforms. This process consists of uniformly infiltrating the preform with a concentrated solution of a precursor in a low viscosity solvent, evaporation of the solvent, introduction of a gaseous second precursor which forms a solid adduct with the first precursor, and then pyrolyzing the adduct to the desired matrix material.

The objective of this work was to evaluate the feasibility of the liquid infiltration approach by deposition of a zirconium carbonitride matrix within a carbon fiber preform. The work plan consisted of two tasks: (1) demonstration of chemical feasibility of forming zirconium carbonitride by pyrolysis of a zirconium tetrachloride/trimethylamine adduct, and (2) initial attempts to apply the chemistry to the formation of zirconium carbonitride within a woven carbon fiber preform. When it was recognized the success would not be achieved with the zirconium carbonitride system using the available equipment, it was decided to demonstrate the principles of the process by depositing hafnium oxide, which is not air sensitive, as the matrix material.

Practical success requires a high solubility of the zirconium tetrachloride precursor in a low viscosity solvent. It was found that the solubility of zirconium tetrachloride in diethyl ether, the solvent of choice according to the literature, was very low. A laboratory search for a suitable solvent demonstrated that acetonitrile was a promising, although not unreactive, solvent.

The solubility of $ZrCl_4$ in acetonitrile is approximately 25% by weight. Dissolution is accompanied by evolution of heat and the solution is very fluid. Evaporation of the solvent yields an off-white solid residue which appears to be a one to two complex or adduct of $ZrCl_4$ with CH_3CN. This complex has the elements needed to form ZrC/ZrN. Attempts to produce ZrC_xN_y by pyrolysis of the complex, however, were not successful.

Passage of trimethylamine through solutions of $ZrCl_4$ in either diethyl ether or acetonitrile did not produce precipitates. Evaporation of these solutions gave solids most of which sublimed during pyrolysis near 300°C. The small amount of residue remaining after heating to 800°C was a mixture of amorphous material and zirconium dioxide.

Passage of ammonia through solutions of $ZrCl_4$ in diethyl ether produced a white precipitate, presumably $ZrCl_4 \cdot 8NH_3$. Similar treatment of solutions of $ZrCl_4$ in acetonitrile also gave a white precipitate. The precipitates from the two solvents were not the same as evidenced by different x-ray diffraction patterns. Further work would be required to establish the exact nature of these products. Pyrolysis of these materials at atmospheric pressure gave extensive sublimation near 300°C and only small amounts of residue at 800°C which again were a mixture of ZrO_2 and amorphous material according to x-ray diffraction analysis. Similar results were obtained using methylamine in place of ammonia or trimethylamine.

An alternative liquid infiltration process was used to successfully deposit hafnium oxide within a woven carbon fiber preform. This process consisted of evacuating the preform, impregnating the preform with a concentrated, low viscosity solution of hafnium methoxide in methanol, evaporation of the excess methanol, and pyrolysis to yield HfO_2 uniformly

distributed throughout the preform. Reiteration of these steps gave increasingly greater amounts of the matrix material throughout the preform. In addition to the inherent value of forming a hafnium oxide matrix, these results indicate that a liquid infiltration process would be practical provided the chemistry is correctly chosen and the processing steps are carefully controlled.

The following were identified as problems which need to be addressed and solved in order to demonstrate feasibility of the liquid infiltration approach to formation of zirconium carbonitride as the matrix within woven fiber preforms.

- The structure of the $ZrCl_4$-acetonitrile adduct needs to be established and its chemistry studied, especially in terms of its pyrolysis before and after reaction with amines.

- The precursors must be kept from contact with atmospheric oxygen and moisture using equipments superior to that available for this study. A high quality stainless steel glove box with continuous gas train purification is absolutely necessary to ensure the high purity oxygen free environment needed to form the ZrC/ZrN complex.

- A pyrolysis vessel capable of pressurization may be needed to suppress sublimation.

INTRODUCTION AND BACKGROUND

The need for materials which can perform under extreme conditions such as high temperatures and hostile environments is well recognized. In general, these materials must have high melting points, resist chemical degradation (oxidation/sulfurdation), and

retain adequate strength/toughness at the operating temperatures. These requirements increasingly point toward the development of ceramic/ceramic composites for structural applications. Ceramic/ceramic composites are typically fiber reinforced. Typical fiber candidates are carbon fibers, SiC fibers, or others. Although carbon fibers possess better mechanical properties than most ceramic fibers at elevated temperatures, they have a severe limitation due to their sensitivity to oxidation. However, for high-temperature applications such as rocket nozzles, where the high strength and high modulus of the best continuous ceramic fibers rapidly deteriorate, coated carbon fibers with a ceramic matrix appear to be the best overall solution.

The best choice for the continuous-fiber components of these composites would be the one that has the best overall high-strength and oxidation resistance. At Applied Sciences, Inc. (ASI) efforts have been directed towards the development of novel, low-cost, carbon-based fibers which have been shown to have superior characteristics of tensile strength, tensile modulus, and oxidation resistance, as well as thermal and electrical conductivity. Carbon fibers of this type are grown in a catalytic process by the pyrolysis of hydrocarbon gas, and are designated by various names such as vapor-grown carbon fiber (VGCF), benzene derived fiber (BDF), and catalytic chemical vapor deposition fiber (CCVD) [1-11]. At ASI and within this report, we refer to this fiber type as VGCF. VGCFs have been shown to have characteristics of electrical and thermal conductivity, strength, and Young's modulus within a range equal to or exceeding the comparable properties of PAN and pitch-based fibers [10]. In addition, VGCFs exhibit superior oxidation resistance to the other commercial PAN and pitch-based fibers [11].

A number of techniques are being developed to produce

ceramic/ceramic composites. These techniques can be classified into chemical vapor infiltration (CVI) process, reaction bonding process, and liquid impregnation process. All these processes have drawbacks. For example:

- Brittle fibers are often damaged during a CVI process due to the applied pressure [12],
- Part size and shape are limited by CVI processing techniques [13-15],
- High temperatures (up to 1600°C) are required to obtain good wetting in a reaction bonding process [16,17],
- Low yield, large shrinkage, and poor phase purity often are associated with the liquid impregnation process [18], and
- None of these processes are particularly conducive to economical and practical scale-up.

In response to the clear need for an effective and efficient process for manufacturing high-performance ceramic/ceramic composites, an evaluation of a new, unique process, Liquid Infiltration (LI), was proposed. This process includes using particular combinations of low-viscosity, liquid and vapor infiltrants, with appropriate pyrolysis programs designed to provide the maximum degree of densification and performance using a minimum number of process cycles. This new route of processing ceramic/ceramic composites has the potential to provide the following advantages:

(1) low-temperature precursor forming chemistry that may allow for ceramic microstructural control,
(2) gentle, pressureless infiltration that does not damage the fiber preforms, thus preserving the structural integrity of the fibers,
(3) high char-volume yields close to theoretical, thereby

fibers were wetted, they were picked up and gently laid, as flat as possible, in the mold. Fibers were aligned longitudinally.

(5) After the desired amount of fibers has been loaded in the mold, the mold piston was placed, and the fibers were pressed to remove as much excess binder as possible, and to compress the fibers to increase the density.

(6) The mold was heated in a furnace at 250 °C for one hour, and then cooled slowly, allowing another hour of heat curing.

(7) After cooling the preform was carbonized in a furnace set to a slow ramp (about 40 degrees C per hour) to 900 °C. When 900 °C was reached, the furnace was cooled down very gradually. The entire process usually took about 24 hours.

(8) After carbonization, the preform was ready for annealing. The annealing was performed at 2900 °C for 10 to 15 minutes in a graphite tube. Density of the artifact was measured after the annealing.

Solubility Studies

Experiments were conducted to find the best solvent for $ZrCl_4$ and to characterize the solid residues remaining after evaporation of the solvents. Measurements were carried out using a variety of solvents (see Table I) as follows. Approximately one-half gram samples of $ZrCl_4$ (sublimed material from Teledyne Wah Chang Albany) were added to preweighed serum vials in a Saranex glove bag. After sealing the vials with Teflon lined silicone septa using aluminum caps, the vials were reweighed to determine the exact amount of $ZrCl_4$ added to each. Solvents were added in 1 mL increments to separate vials until dissolution occurred or it became evident that the $ZrCl_4$ was not dissolving to any significant extent. It was noted whether or not heat was evolved or absorbed, if color or viscosity changes occurred, and if changes happened immediately or over an extended period of time.

TABLE I. Solubility of $ZrCl_4$ in Various Solvents

Solution Number	Solvent	Solubility (g/100 cc)	Comments
1	Diethyl ether	0.4	
2	Dimethoxyethane	8	b
3	Tetrahydrofuran	8	c
4	Dimethoxytetra-hydrofuran	10	b
5	1,3-Dioxolane	-	a
6	Methoxyethyl ether		a
7	Toluene	-	a
8	Acetonitrile	25	
9	Methylene chloride	-	a
10	Dimethylformamide	-	a
11	Methyl ethyl ketone	-	a
12	Acetone	-	a
13	Titanium tetrachloride	-	a
14	Dimethyl sulfoxide	-	a
15	Diethylamine	-	a
16	Triethylamine	-	a

a. Very low solubility.
b. The liquids turned brown and became thicker.
c. The liquid turned pink and thicker.

Larger quantities were dissolved in the most promising solvents using round bottom flasks with stopcocks and adapters so that evaporation of the solvent could be done under varying conditions and the residues examined. The solid remaining after evaporating the solvent (acetonitrile) from solution 8 was characterized by an x-ray diffractometer.

The ZrC/ZrN System

The experiments were performed without fiber preform in an attempt to form ZrC/ZrN. The procedures included forming solid precursors first and then pyrolyzing the solid precursors. After pyrolysis, selected specimens were analyzed by X-ray diffraction and Auger electron spectroscopy.

(A) Precursor Formation

Various routes were taken to obtained the solid precursors. Table II summarizes the experimental matrix of precursor formation procedures.

(B) Pyrolysis of Precursors

The precursors were pyrolyzed under different atmospheres. The pyrolysis was conducted in a tube furnace. The furnace was preheated to the desire temperatures before the specimens were loaded. It took normally less than 10 minutes for the specimens to reach the desired temperatures. When a gas was involved in the pyrolysis, the specimens were flushed with the gas for 15 minutes at room temperature prior to the pyrolysis. Figure 1 shows a schematic of the pyrolysis setup. The experimental conditions of the pyrolysis are given in Table III. After the pyrolysis, X-Ray analysis was performed.

TABLE II. Experimental Matrix of Precursor Formation

Precursor Designation	Type	Procedure
A	Precipitate (Adduct)	Bubbling NH_3 into Et_2O solution (0.3% $ZrCl_4$)
B	Residue	Evaporation* of CH_3CN solution (20% $ZrCl_4$)**
C	Adduct	Pass NH_3 thru residue from CH_3CN solution
D	Adduct	Pass TMA thru residue from CH_3CN solution
E	Residue	a. Pass TMA into CH_3CN solution b. Evaporate solution
F	Residue	a. Pass MMA into CH_3CN solution b. Evaporate solution

* All solutions were evaporated under vacuum at room temperature.
** All acetonitrile solutions contained 20% $ZrCl_4$.

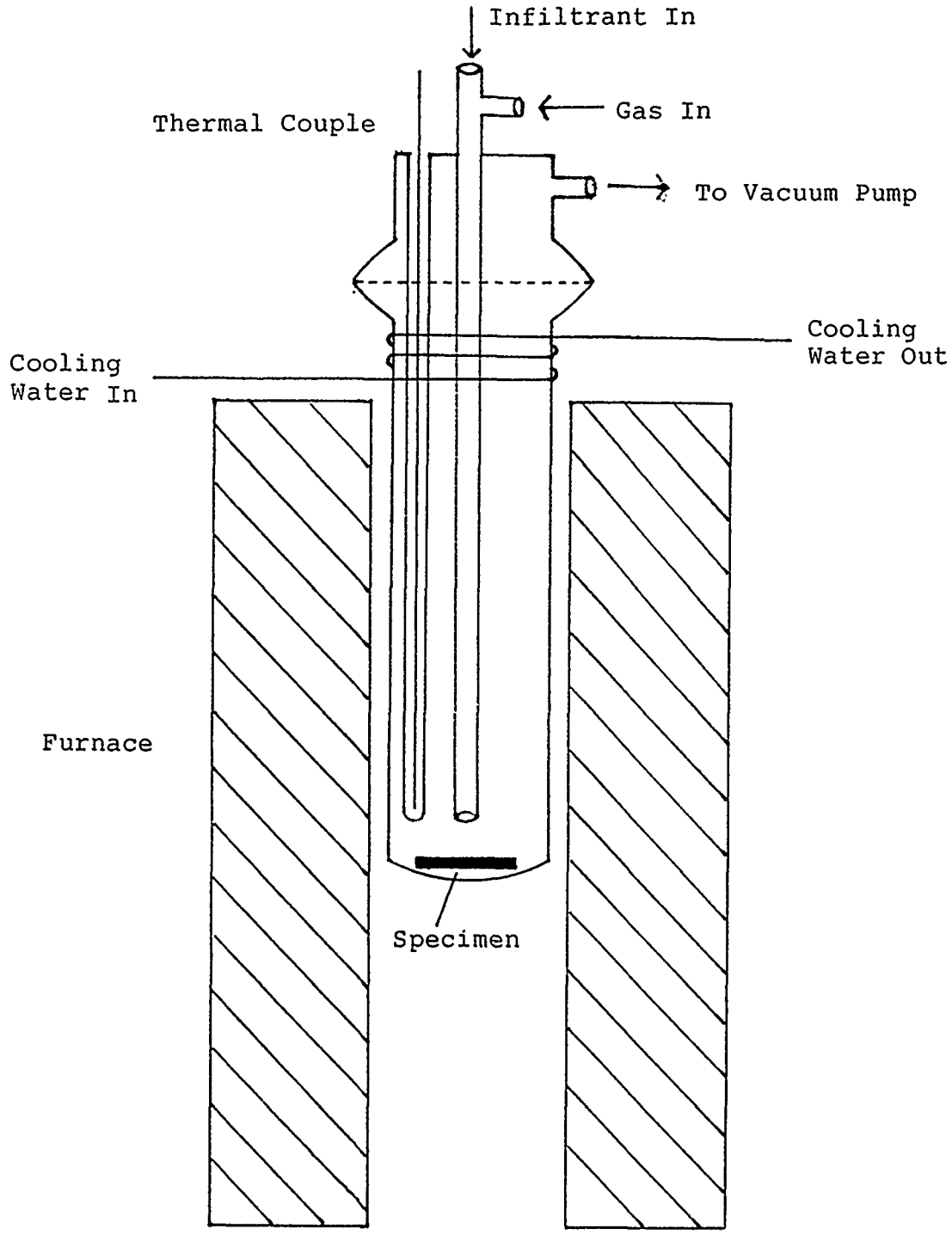

Fig. 1. A scematic showing the pyrolysis setup.

TABLE III. Pyrolysis Conditions

ID Number	Precursor Designation	Atmosphere	Temperature (°C)	Duration (min.)
1	A	NH_3 + H_2 1/1	820	10
2	B	NH_3	835	15
3	B	NH_3 + Ar 1/1	860	15
4	C	Vacuum	840	15
5	C	NH_3	815	10
6	C	N_2	835	15
7	E	NH_3	855	15
8	E	TMA	820	10
9	E	N_2	820	10
10	F	MMA	810	10

The HfO_2 System

The experiments were conducted in an attempt to obtain HfO_2 using the same concept as in the ZrC/ZrN system. Solutions containing $HfCl_4$ and methyl alcohol solvent were evaporated to collect the solid residuals. These residuals were then pyrolyzed under vacuum at 800 °C. The products were analyzed by an X-Ray Diffractometer.

Preform Infiltration

Due to reasons discussed later, the only infiltration of a fiber preform was conducted to yield hafnium oxide matrix. The precursors were the residuals from solutions containing $HfCl_4$ and methyl alcohol solvent. The experimental procedures are as follows.

Step 1. Dissolve $HfCl_4$ into methyl alcohol solvent.
Step 2. Evacuate the chamber containing preform.
Step 3. Infiltrate the solution into the preform at room temperature.
Step 4. Vacuum dry leaving solid residual distributed onto fiber surface and throughout the preform interstices.
Step 5. Pyrolyze the specimen to form HfO_2 matrix in the preform interstices.

Three experiments were carried out. The first experiment had a solution of 30% concentration, and went through only one cycle of infiltration. The preform was not subjected to vacuum prior to the infiltration. The second experiment also had a solution of 30% concentration, and Step 2 through 5 were repeated 3 times. The third experiment used a solution containing 100 g of $HfCl_4$ per 100 g of methanol, and step 2 to Step 5 were repeated 8 times. The specimens in the second and the third cases were

evacuated before the infiltration. Each specimen was weighed after every cycle to determine the weight gain. The specimens in all the cases were taken from the same fiber preform with a density of 1.17 mg/cm^3. After infiltration and pyrolysis, the specimens were broken by hand, and the cross sections were examined by Scanning Electron Microscopy (SEM) and Energy Dispersion Analysis of X-ray (EDAX).

RESULTS AND DISCUSSION

Solvent Selection

Although the literature indicates that $ZrCl_4$ is soluble in diethyl ether[19], we found this solubility to be only about 0.4%. This is not sufficient for a practical infiltration process. Thus a search for a better solvent was undertaken. It can be seen from the results shown in Table I that $ZrCl_4$ does not dissolve to any appreciable extent in most of the solvents. It had significant solubility only in dimethoxyethane, tetrahydrofuran, dimethoxytetrahydrofuran, and acetonitrile (solutions 2,3,4, and 8 in Table I). Solutions 2, 3, and 4 were rejected due to their high viscosity which increased upon standing. $ZrCl_4$ appears to catalyze polymerization of these solvents.

The solubility tests indicated that the most promising solvent was acetonitrile, CH_3CN, providing high solubility and a low viscosity solution. Both properties are valuable for a liquid infiltration process. Heat is evolved during dissolution of $ZrCl_4$ in acetonitrile indicating the possibility of strong solvent/solute interaction, possibly adduct formation. This possibility was investigated by removing the excess acetonitrile leaving a white solid residue. The weight of this residue

exactly matched that calculated for the addition of two molecules of acetonitrile to $ZrCl_4$ giving $ZrCl_4 \cdot 2CH_3CN$. The x-ray diffraction pattern of this solid confirmed that it was not $ZrCl_4$, but did not correspond to any known pattern. Further work would be required to establish the structure of this product.

In addition to working with acetonitrile solutions of $ZrCl_4$, diethyl ether was used as the solvent in some experiments to allow comparison with published information.

Precursor Formation

In order to prepare ZrC/ZrN as a matrix material, precursors containing both carbon and nitrogen in addition to Zr are required. It was hoped that addition of an amine such as trimethylamine (TMA) to a $ZrCl_4$ solution would yield a solid adduct which could be pyrolyzed without melting or volatilizing to give the desired matrix material. It was found that addition of TMA to solutions of $ZrCl_4$ in either acetonitrile or diethyl ether did not yield precipitates. Evaporation of such solutions did leave solid residues, the pyrolysis of which is discussed in the next section.

Six types of precursor were formed as summarized in Table II. The first, designated as A in the table, appears to be $ZrCl \cdot 8NH_3$, in agreement with data in the literature [19]. The rest of the precursors were all produced from the residual of acetonitrile solutions (20% $ZrCl_4$). They are described below with reference to the table.

Precursor A: White precipitates were obtained upon bubbling ammonia into diethyl ether solutions of $ZrCl_4$. X-ray diffraction patterns of the residues did not match existing standard patterns. These products were considered to be $ZrCl_4 \cdot 8NH_3$ as

described in the literature [20].

Precursor B: This material is considered to be $ZrCl_4 \bullet 2CH_3CN$ as discussed previously.

Precursor C: Upon passing ammonia to the residue from the acetonitrile solution, heat evolved immediately. Based on the weight increase and assuming that ammonia replaced the acetonitrile, it was speculated that the adduct was $ZrCl_4 \bullet 6NH_3$.

Precursor D: Upon passing TMA to the residual from acetonitrile solution, liquid appeared and the solid turned brown. The precursor, having a weight corresponding to $ZrCl_4 \bullet 3.2N(CH_3)_3$, was obtained after removing the liquid under vacuum.

Precursor E: The clear, colorless acetonitrile solution turned yellow, and then orange, light brown, reddish brown, and finally dark reddish brown when TMA was introduced. Meanwhile, heat evolved. No precipitate was formed. After evaporation of solvent, a dark reddish brown precursor, having a weight corresponding to $ZrCl_4 \bullet 1.5N(CH_3)_3$, was obtained.

Precursor F: Heat evolved and the liquid turned yellow when MMA bubbled into acetonitrile solution. The yellow precursor (possibly $ZrCl_4 \bullet 8CH_3NH_2$) was obtained after removing the liquid.

Pyrolysis of Precursors

The precursors were pyrolyzed under various atmospheres as shown in Table III. The precursor designations in Table III correspond to those from Table II. The common results are that most of the solids sublimed at approximately 300°C, and the products were powders. There powders were subjected to x-ray diffraction analysis. The results, as shown in Table IV, indicate that all

the products contained zirconium oxide. In some cases, $ZrCl_2$, $ZrH_{0.6}N$, and ZrClN were found. It is noted that these products were obtained only in the cases where TMA or MMA was involved. The weight loss of each precursor after pyrolysis are also listed in Table IV. As can be seen, the weight loss due to subliming was at least 67% and could be as much as 93%. One of the sublimed materials which was analyzed by x-ray diffraction was found to be NH_4Cl.

The fact that oxide was found in all of the products demonstrates that strict isolation from air and moisture was not maintained throughout processing. Exposure to oxygen and moisture was due at least in part to the use of dry bags, which do not maintain a sufficiently inert atmosphere. An absolutely inert atmosphere is required for work with materials as sensitive to air and moisture as $ZrCl_4$ and its amine adducts. Purchase and setup of a stainless steel glove box would be needed.

Formation of $ZrCl_2$ and $ZrH_{0.6}N$ were confirmed by x-ray diffraction. Formation of ZrClN is listed for samples 2 and 3 in Table IV because the yellow color of the product and the pyrolysis conditions are consistent with the reported formation of ZrClN by pyrolyzing $ZrCl_4 \bullet xNH_3$ [20]. Possible reactions leading to the non-oxide products are proposed below.

Condition 1:

$$ZrCl_4 \cdot 8NH_3 \xrightarrow{NH_3 + H_2} ZrCl_4 \cdot 2NH_3 + 6NH_3$$

$$ZrCl_4 \cdot 2NH_3 + H_2 \xrightarrow{NH_3 + H_2} ZrCl_2 + 2NH_4Cl$$

Condition 2:

$$ZrCl_4 \cdot 2CH_3CN \xrightarrow{NH_3} ZrCl_4 \cdot xNH_3$$

$$ZrCl_4 \cdot xNH_3 \xrightarrow{NH_3} ZrClN + HCl$$

Condition 3:

$$ZrCl_4 \cdot 2CH_3CN \xrightarrow{NH_3 + Ar} ZrCl_4 \cdot xNH_3$$

$$ZrCl_4 \cdot xNH_3 \xrightarrow{NH_3 + Ar} ZrClN + HCl$$

Condition 4:

$$ZrCl_4 \cdot 6NH_3 \longrightarrow ZrCl_4 \cdot 2NH_3 + 4NH_3$$

$$ZrCl_4 \cdot 2NH_3 \longrightarrow ZrH_{0.6}N$$

Condition 5:

$$ZrCl_4 \cdot 6NH_3 \xrightarrow{NH_3} ZrCl_4 \cdot 2NH_3 + 4NH_3$$

$$ZrCl_4 \cdot 2NH_3 \xrightarrow{NH_3} ZrH_{0.6}N$$

Condition 6:

$$ZrCl_4 \cdot 6NH_3 \xrightarrow{N_2} ZrCl_4 \cdot 2NH_3 + 4NH3$$

$$ZrCl_4 \cdot 2NH_3 \xrightarrow{N_2} ZrCl_2$$

TABLE IV. Pyrolysis Results (weights are in grams)

ID Number	Initial Weight	Final Weight	Weight Loss	% Weight Loss	Products	Color
1	1.082	0.356	-0.726	67.1	ZrO_2, $ZrCl_2$	Gray
2	1.47	0.28	-1.19	81.0	ZrO_2, (ZrClN)*	Yellow
3	1.25	0.11	-1.14	91.2	ZrO_2, (ZrClN)*	Yellow
4	1.31	0.18	-1.13	86.1	ZrO_2, $ZrH_{0.6}N$	Greenish
5	1.307	0.200	-1.107	84.5	ZrO_2, $ZrH_{0.6}H$	Dark Green
6	1.368	0.207	-1.160	84.9	ZrO_2, $ZrCl_2$	Dark Yellow
7	0.62	0.12	-0.50	80.7	ZrO_2	Black
8	1.511	0.271	-1.280	82.5	ZrO_2	Black
9	1.548	0.215	-1.333	86.1	ZrO_2	Black
10	1.1.1	0.073	-1.028	93.4	ZrO_2	Black

* ZrClN was not confirmed by x-ray diffraction. See text for explanation.

The Formation of Hafnium Oxide by the Liquid Infiltration Process

(A) Justification

Due to subliming during pyrolysis as well as the oxygen/moisture sensitivity associated with the zirconium tetrachloride/amine systems, HfO_2 was chosen as the matrix material in order to demonstrate the basic infiltration technique. The reasons for using hafnium oxide are as follows.

- The same liquid infiltration procedures can be carried out to yield carbon fiber reinforced hafnium oxide matrix composite.
- The material system is not as sensitive to oxygen/moisture as $ZrCl_4$, and therefore sophisticated systems are not required.
- Hafnium oxide has been suggested to be one of the possible matrix materials for high-temperature ceramic/ceramic composites.

Therefore, liquid infiltration experiments were conducted using $HfCl_4$ and methyl alcohol to form the infiltrant, followed by evaporation of methanol, and pyrolysis to yield the hafnium oxide matrix material as described in the experimental section.

(B) Solubility and Pyrolysis

The solubility of $HfCl_4$ in methyl alcohol was determined to be > 125 g/100 cc. After evaporation of the methanol solvent, the residual was pyrolyzed under vacuum to yield hafnium oxide, as determined by X-Ray diffraction.

TABLE V. Weight Increase in Grams Due to Infiltration of Hafnium Oxide

ID Number	27	50	51
g $HfCl_4$/100g MeOH	30	30	100
Preform Init. Wt.	0.150	0.288	0.249
Weight No. 1 Increment % Increase	0.163 0.013 (7.98%)	0.325 0.037 (12.85%)	0.316 0.067 (26.91%)
Weight No. 2 Increment		0.385 0.033	0.387 0.071
Weight No. 3 Increment		0.389 0.031	0.470 0.083
Weight No. 4 Increment			0.548 0.078
Weight No. 5 Increment			0.619 0.071
Weight No. 6 Increment			0.697 0.078
Weight No. 7 Increment			0.776 0.079
Weight No. 8 Increment			0.856 0.080
Total Wt. Gain	0.013g (7.98%)	0.137g (47.57%)	0.617 (247.79%)

(C) The Liquid Infiltration Process

Specimens were processed by in three different conditions. The weight gains due to infiltrations are given in Table V. After the first cycle, specimen 27 (see Table V) had the lowest percentage weight gain and specimen 51 had the highest percentage weight gain. As shown in the table, the weight continuously increases and the increment after each cycle remains the same. Obviously, a high-concentration infiltrant gives a higher yield of precursor and evacuating the specimen prior to the infiltration helps fill the interstices with infiltrant. The cross section of each sample was examined by an SEM, and the results are shown in Figures 2, 3, and 4 respectively. The EDAX analysis (Fig. 5) on these cross section indicated that hafnium was detected throughout the cross section. EDAX dot mapping on thes ecross sections, as shown in Figure 6, proved that specimen with higher weight gain indeed had more hafnium oxide in its interstices.

As shown in Table V and Figure 6, the infiltrant not only successfully entered the interstices of specimens, it did so to give a uniform distribution of hafnium throughout the specimens. Another encouraging result is that after several processing cycles, no surface-blockage occurred as has been observed with Chemical Vapor Infiltration (CVI). The preform used had a density of 1.17 g/cm^3, corresponding to a porosity of 48% (taking 2.25 g/cm^3 as the theoretical density of carbon). If the all the porosity was to be filled, the final percentage weight increase due to infiltration would be 396% (taking 9.28 g/cm^3 as the theoretical density of hafnium oxide). In the case where the specimen was infiltrated eight times, the percentage weight gain was 248%. Thus, 63% of the porosity has been filled with the hafnium oxide matrix. At this point, no sign of surface-block was observed as indicated by the steady weight increment. This led to the result that no density gradient was built (as

indicated by the EDAX mapping). This would be one of the major advantages to the CVI process. Although we were not able to carry out the ZRC/ZrN system, the novel, unique Liquid Infiltration process was demonstrated satisfactorily by using HfO_2, a highly promising matrix material for high-temperature ceramic/ceramic composites.

Fig. 2. An SEM photo of the cross section of Specimen 27.

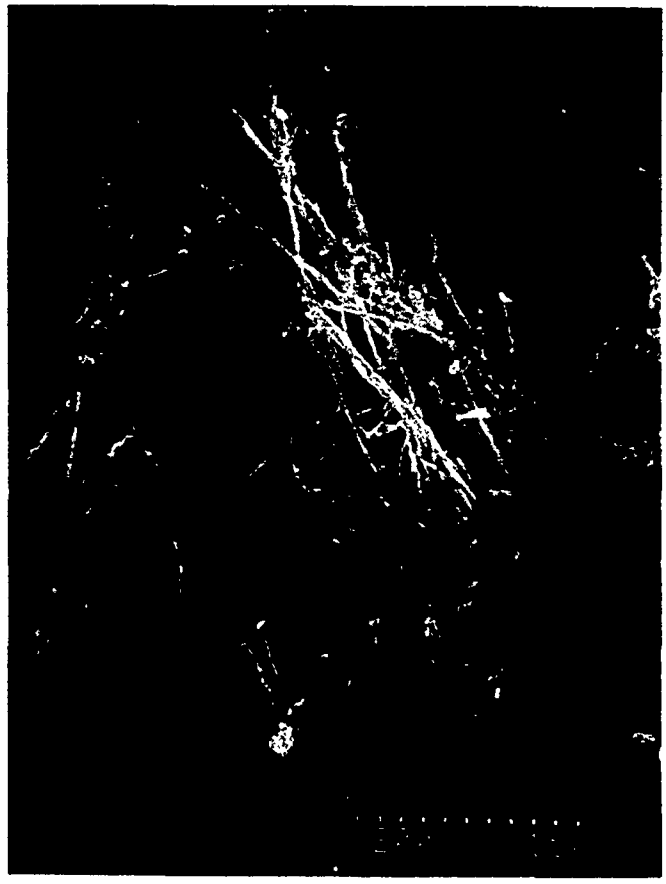

Fig. 3. An SEM photo of the cross section of Specimen 50.

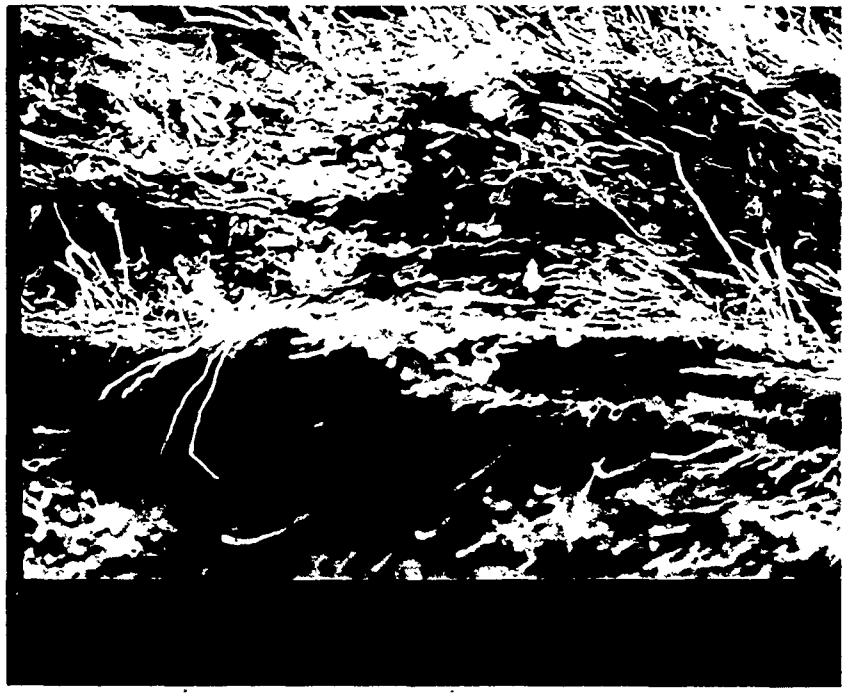

Fig. 4. An SEM photo of the cross section of Specimen 51.

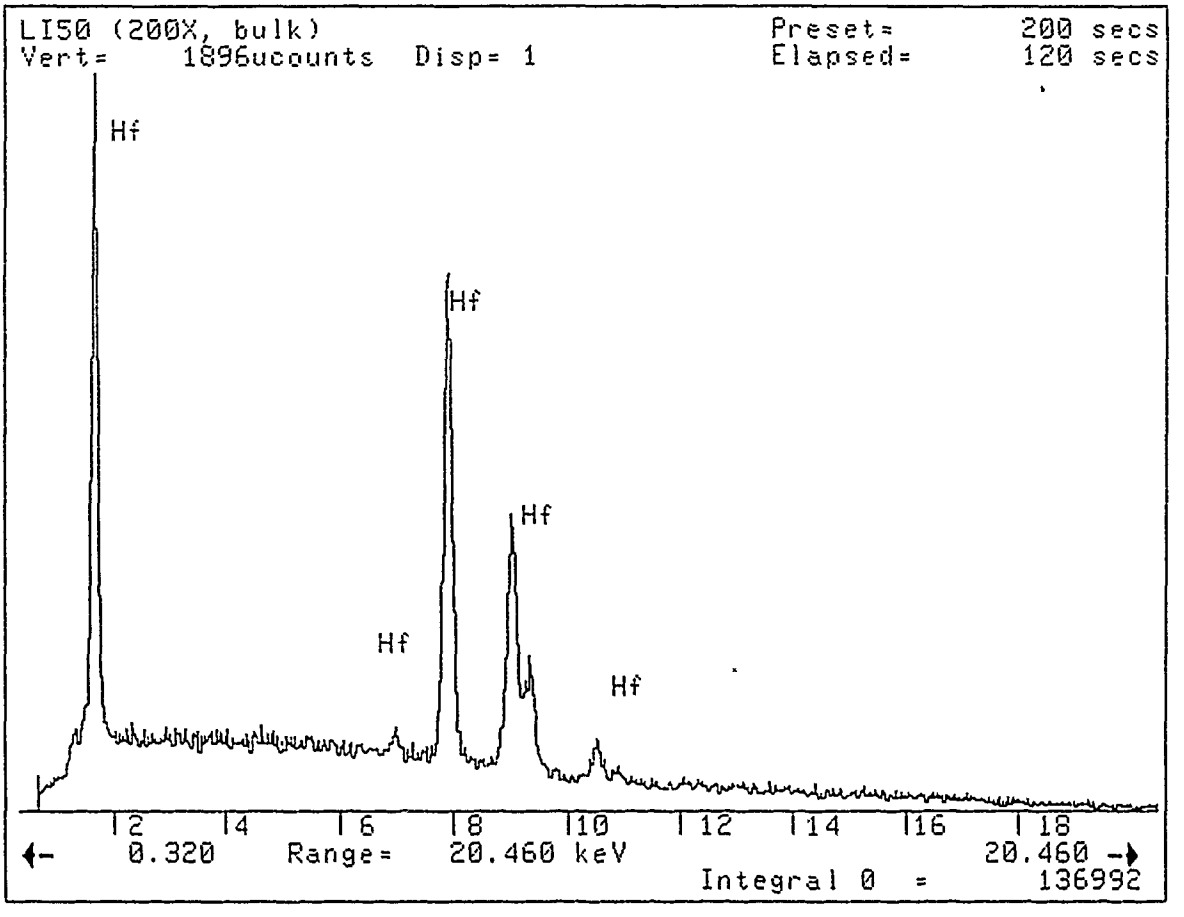

Fig. 5. EDAX analysis on the cross section of hafnia matrix specimen showing Hf peaks.

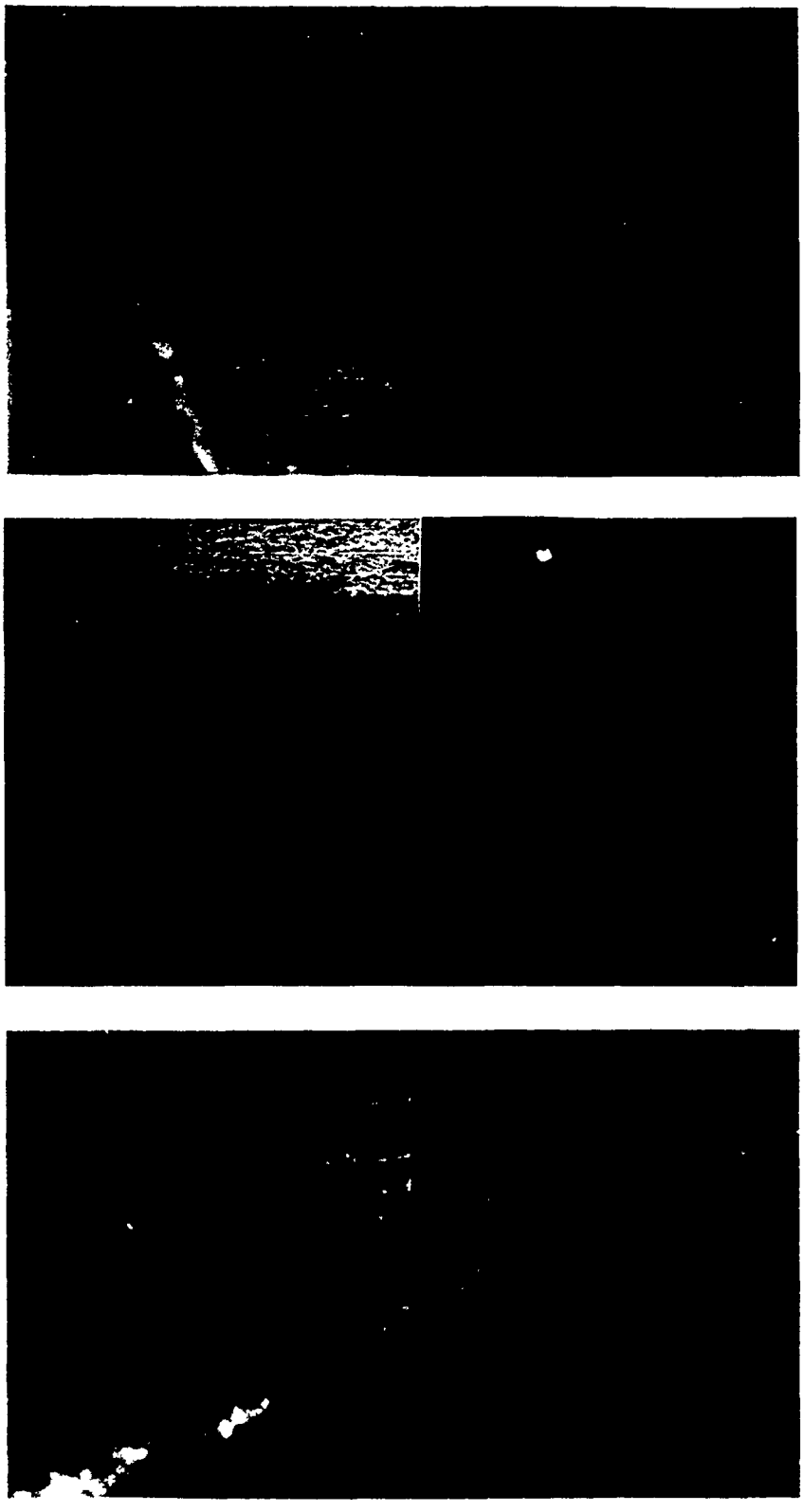

Fig. 6. EDAX dot mapping of (a) specimen 27, (b) specimen 50, and (c) specimen 51.

CONCLUSIONS

The following conclusions can be drawn from this study.

1. Extensive study of the zirconium carbonitride system was quite instructive in determining key parameters needed to allow for successful liquid infiltration processing leading to advanced ceramic composites. These were found to be the availability of solvents for the precursor infiltrant constituent, and the potential sensitivity of this type of processing to moisture and air. In the case of zirconium system, $ZrCl_4$ was found to have an impractically low solubility for the originally proposed solvent. A solvent (acetonitrile) was successfully identified, but generated an air- sensitive precursor with low subliming temperature. This result, together with the fact that $ZrCl_4$ is also highly air and moisture sensitive, made the demonstration of liquid infiltration difficult within the limit of time and facilities available.
2. Difficulties with the zirconium carbonitride system were more than offset by the ease and efficiency of densifying preforms with hafnium oxide using the proposed liquid infiltration technique. Uniform distribution of HfO_2 matrix material within VGCF preforms is indicated by the uniform hafnium distribution in the samples after filling 63% of the preform porosity during 8 infiltration cycles. These promising results are due to the high solubility of hafnium tetrachloride in methanol, the low viscosity of these solutions, the lack of air sensitivity of the system, and the ease of pyrolysis of the precursor to the desired hafnium dioxide.
3. The liquid infiltration methodology technique proposed for study under the current Phase I research program shows high promise for producing advanced ceramic matrix materials with no damage to the reinforcement. Additionally it provides an

economical path to produce ceramic composites due to the high yield and the relative low processing temperatures.

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